Supporting Information for: Magnetism in metal-organic capsules

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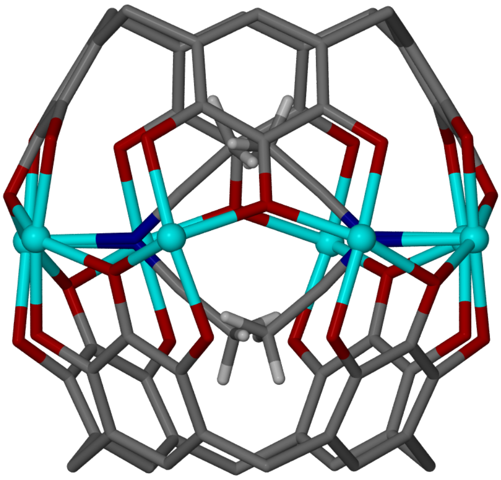


Figure S1. The two disordered positions for both MeCN molecules within the cavity of **2**.

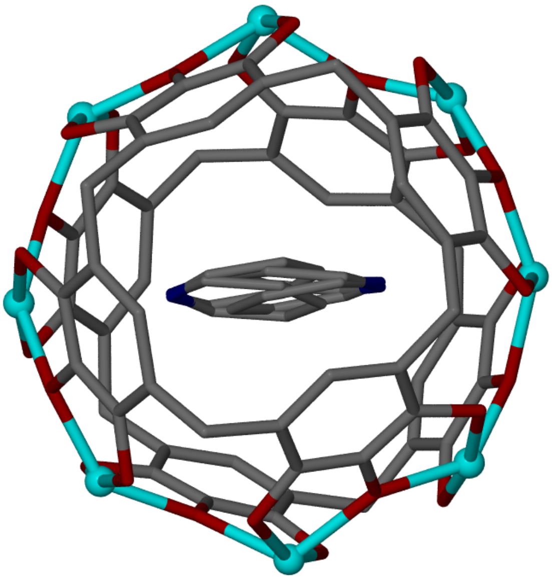


Figure S2. The four disordered pyridine positions within the cavity of **3** indicating the weak interaction with Co centers that are opposite one another within the capsule.

Computational Details

Density functional theory (DFT) calculations were performed on the model complexes to determine the relative energies of the lowest singlet and triplet states. Exploratory computations using a variety of exchange correlation (xc) functionals showed that the ordering and singlet-triplet energy gap was insensitive to nature of the xc-functional used; therefore below we only quote the results using the hybrid PBE1PBE functional. The one-electron basis set consisted of the Stuttgart-Dresden SDD effective core (pseudo) potential basis set on the nickel, and the 6-311G* basis on all other atoms. Spin-unrestricted calculations were performed for the triplet state and for all model complexes spin-contamination was found to be negligible. For the singlet state spin-restricted calculations were performed. For the five-coordinate model complex it was checked that a spin-unrestricted calculation on the singlet (started from a broken symmetry guess) collapsed to the restricted solution of the Kohn-Sham equations. In addition for the five-coordinate model complex complete active-space self-consistent-field (CASSCF) calculations were performed. The active space was constructed as 8 electrons distributed in 10 orbitals (five primarily *3d* orbitals centered on Ni, plus their five antibonding counterparts containing an extra node in the metal-ligand region) giving 30240 configuration state functions. This type of active space has previously been shown to give good geometries and energies for open-shell metal complexes.[S1] All computations were performed using the *Gaussian 03* program. [S2]

References:

S1. M. J. Paterson, P. A. Hunt, M. A. RobbOhgi Takahashi, *J. Phys. Chem. A*, **2002**, *106*, 10494 – 10504; G. A. Worth, G. Welch, M. J. Paterson, *Mol. Phys.* **2006**, *104*, 1095 - 1105.

S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, (Revision D.01),* 2004.

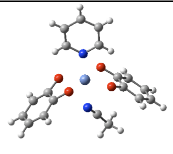
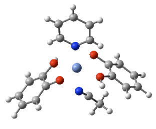
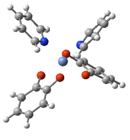
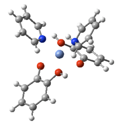
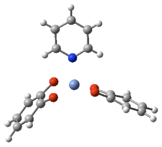
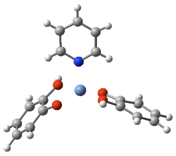
	Method	$\Delta E_{S/T}$ / eV *
 *Oh 1*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	2.02
 *Oh 1 – 2H*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	1.99
 *Oh 2*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	2.81
 *Oh 2 – 2H*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	2.07
 *SP*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	1.61
	CASSCF(8,10) Ni – SDD N, O, C, H – 6-31G*	1.64
 *SP – 2H*	PBE1PBE Ni – SDD N, O, C, H – 6-311G*	2.05

Table S1. Calculated energy differences in singlet vs triplet states for the various Ni environments present within **2** both with and without hydrogen atoms on catechol ligands that represent fragments of the capsule seam. *Oh* = octahedral, *SP* = square planar.

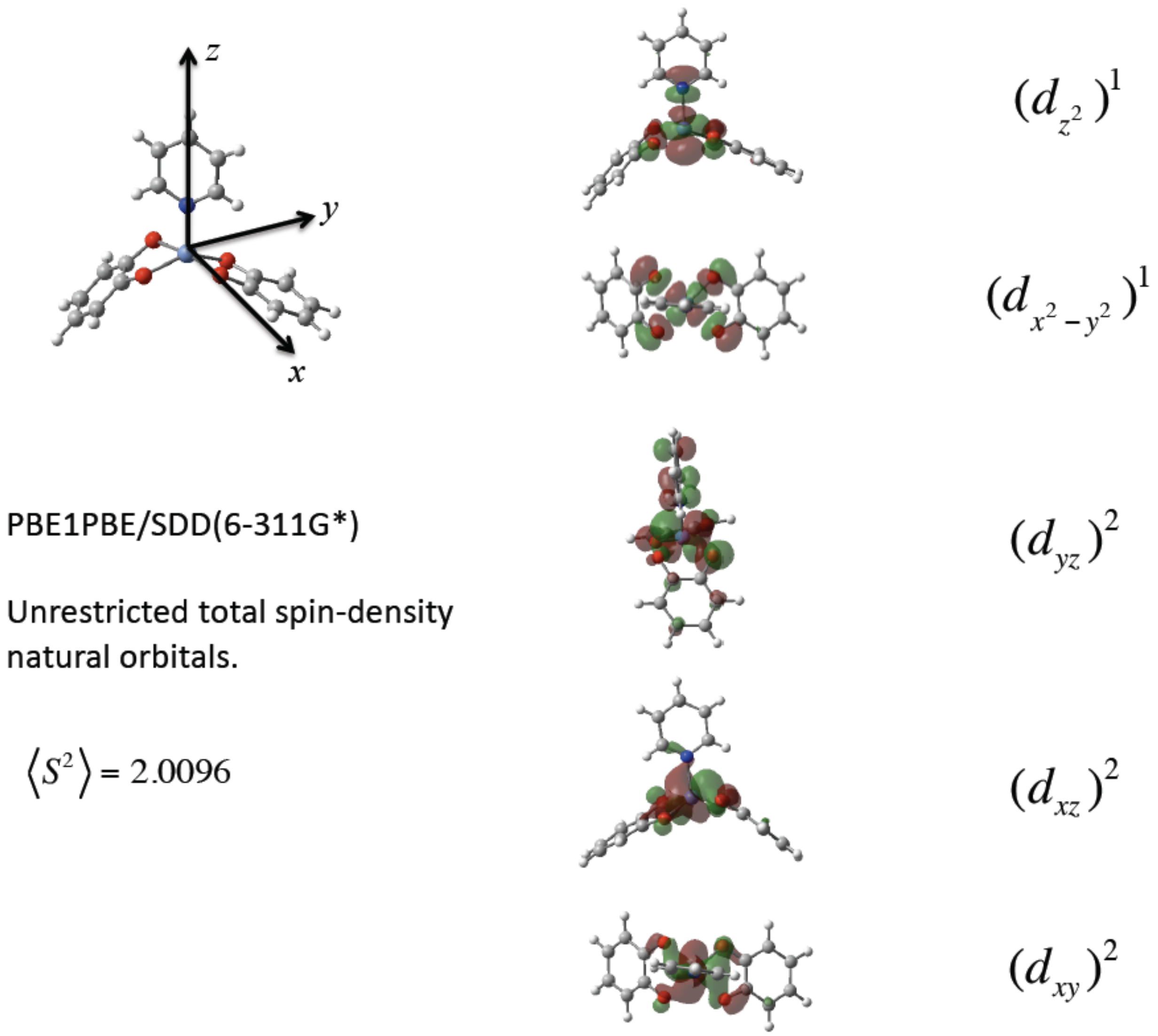


Figure S3. Unrestricted total spin-density natural orbitals for calculations described above.